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(54) STEEL MATERIAL EXCELLENT IN TEMPER EMBRITTLEMENT RESISTANCE AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To improve temper embrittlement at hot working for a low alloy steel of specific composition by subjecting this steel to secondary deoxidizing refining succeeding slight-degree deoxidation and then adding REM, Y, and Zr and forming their solid solutions.

CONSTITUTION: At the time of tapping a molten steel, having a composition containing, by weight, 0.02-0.40% C, 0.01-0.60% Si, 0.30-2.0% Mn, $\leq 0.025\%$ P, $\leq 0.010\%$ S, $\leq 0.0060\%$ N, and $\leq 0.003\%$ O and containing one or ≥ 2 kinds among specific weight percentages of Cu, Ni, Cr, Mo, W, Nb, V, B, and Ta, from a steelmaking furnace, slight-degree deoxidizing treatment is done by adding Si, Mn, etc. Successively, at the time of secondary refining, secondary deoxidizing refining is done by the addition of Al, Ca, Ti, etc., and then adding one or ≥ 2 kinds among REM, Y, and Zn by 5-200ppm to form the solid solutions of them by 1-50ppm in the steel material. By this method, the material can be prevented from embrittling at the time of subjecting a steel stock, prepared by hot-rolling a slab of this steel, to working into various structure and to tempering treatment and also during use of these structures at high temp.

CLAIMS

[Claim(s)]

[Claim 1] By weight %, C:0.02 - 0.40%, Si:0.01-0.60%, Mn: 0.30-2.0%, P<=0.025%, S<=0.010%, They are the steel materials which contained N<=0.0060% and O<=0.0035%, contained REM:5-200ppm, Y:5-200 ppm and Zr:5-200 ppm % of a kind or, and two sorts or more further, and were excellent in the tempering-proof brittleness characterized by the remainder consisting of Fe and an unescapable impurity.

[Claim 2] The steel materials excellent in the tempering-proof brittleness according to claim 1 characterized by containing a kind (aluminum:0.010-0.20%, Ti:0.005-0.08%, and calcium:0.001-0.05%) or two sorts or more, and dissolution REM:1-50ppm, Y:1-50 ppm of dissolution, a dissolution Zr:1-50ppm kind, or two sorts or more existing in the state of dissolution in steel by weight %.

[Claim 3] The steel materials excellent in the tempering-proof brittleness according to claim 1 or 2 characterized by containing a kind (Cu:0.05-2.0% and nickel:0.05-10.0%) or two sorts and/or Cr:0.05-10.0%, Mo:0.05-2.0%, W:0.05 - 3.0%, Nb:0.005-0.10%, and V:0.01 - 0.40% of a kind or two sorts or more, and/or B:3-30 ppm by weight %.

[Claim 4] The steel materials excellent in tempering-proof brittleness given in claims 1 and 2 characterized by containing Ta:0.005-0.40% by weight %, or any 1 term of 3.

[Claim 5] It faces manufacturing the steel which has the component of a publication in claims 2 and 3 or any 1 term of 4. By secondary refining which follows ***** this deoxidation [weak] immediately after the weak deoxidation which adds Si or Mn at the time of tapping, or the weak deoxidation which adds a part of aluminum, aluminum, The manufacture approach of steel materials excellent in the tempering-proof brittleness characterized by adding a kind of REM, Y, and Zr, or two sorts or more after adding a kind of Ti and calcium, or two sorts or more, and carrying out hot working after casting.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to low alloy steel excellent in tempering-proof brittleness, and its manufacture approach. It is related with control of embrittlement during the embrittlement by the postweld heat treatment at the time of steel-materials processing to the structures, such as the embrittlement at the time of heat treatment of the low alloy steel manufactured by rolling, forging, and casting in detail and a pressurized container using the steel materials, a chemistry container, a bridge, a machine part, and the offshore structure, (and annealing of bending workpiece, stress relieving annealing, etc.), or the use at the time of elevated-temperature use.

[0002]

[Description of the Prior Art] According to the advance of chemical technology, the chemical reaction container, the pressurized container, etc. are what also has the still severer environment which tends to be enlarged gradually and used in recent years. Therefore, the actual condition is that the demand to the property required of steel materials and control of tempering brittleness above all becomes very severe by long-duration-izing of the postweld heat treatment (stress relieving annealing) accompanying heavy-gage-izing of steel materials, and elevated-temperature-ization of service temperature, and the cure is difficult.

[0003] As a Prior art which controls tempering brittleness and hydrogen embrittlement, JP,55-91962,A, JP,56-58952,A, and JP,57-29553,A have the proposal of a publication. Moreover, as a conventional technique which adds Dissolution REM, Dissolution Y, and Dissolution Zr, there is a proposal by Japanese Patent Application No. No. 198830 [six to]. A proposal given in JP,55-91962,A makes nickel system heat treated steel contain dissolution metallic aluminum 0.15% or more, and aims at an improvement a tempering-proof brittle one and brittle [waterproof] by the site competition of Si and Dissolution aluminum in a grain boundary.

[0004] A proposal given in JP,56-58952,A improves tempering-proof brittleness by making the low alloy steel of a specific component contain the amount of limitation more than the amount consumed by the inside S of steel of Zr or calcium. A proposal given in JP,57-29553,A improves tempering-proof brittleness by making the low alloy steel of a specific component contain 20-100 ppm of calcium.

[0005] By adding REM, Y, or Zr to the low alloy steel of a specific component, and limiting those amounts of dissolution to it, the proposal in Japanese Patent Application No. No. 198830 [six to] controls generating of a hydrogen nature defect, and improves the internal quality of steel materials.

[0006]

[Problem(s) to be Solved by the Invention] The publication which improves tempering brittleness does not have about [that publication that the tempering brittleness of nickel system heat treated steel is improved by dissolution metallic aluminum does not have the indication of the technique about REM Y, and Zr of a certain thing], Dissolution REM, Dissolution Y, and Dissolution Zr in JP,55-91962,A. Therefore, the technical thought which solves said technical problem is not contained at all, but the actual condition is that said technical problem is left as it is.

[0007] Although JP,56-58952,A has the publication by which the tempering-proof brittleness of low alloy steel is improved with the amount of limitation more than the amount consumed by the inside S of steel of Zr or calcium, the thought which compensates consumption of Zr by O and N also about about [that there is no indication of the technique about REM and Y] and Zr is missing, and there is no publication that Dissolution REM, Dissolution Y, and Dissolution Zr improve the tempering-proof brittleness of low alloy steel. Therefore, the technical thought which solves said technical problem is not contained at all, but the actual condition is that said technical problem is left as it is.

[0008] The publication which improves tempering-proof brittleness does not have about [that the publication by which the tempering-proof brittleness of low alloy steel is improved by calcium does not have the indication of the technique about REM, Y, and Zr of a certain thing], Dissolution REM, Dissolution Y, and Dissolution Zr in JP,57-29553,A. Therefore, the technical thought which solves said

technical problem is not contained at all, but the actual condition is that said technical problem is left as it is.

[0009] The publication by which the internal division quality of low alloy steel is improved by Japanese Patent Application No. No. 198830 [six to] with the amount of limitation more than the amount consumed by the inside S, O, and N of the steel of REM, Y, and Zr A certain thing, About [that there is no indication of the technique about tempering-proof brittleness], REM, Y, The thought by which there is no limitation of O and N which compensate consumption by O and N also about consumption of Zr in a claim, and it controls the amount of dissolution strictly is inadequate, and there is no publication to which Dissolution REM, Dissolution Y, and Dissolution Zr improve the tempering-proof brittleness of low alloy steel. Therefore, the technical thought which solves said technical problem is not contained at all, but the actual condition is that said technical problem is left as it is.

[0010] This invention aims at easing the component constraint of impurities, such as P, or Si about tempering brittleness further, and enlarging the degree of freedom of a component design while it improves sharply the tempering-proof brittleness and the hydrogen embrittlement-proof in the above mentioned low alloy steel.

[0011]

[A means to solve invention] When this invention person etc. investigated minutely about the tempering brittleness of low alloy steel, the amount of dissolution of REM, Y, and Zr and tempering-proof brittleness which dissolve in steel newly came to carry out the knowledge of also improving hydrogen embrittlement while having very close relation. The place made into the summary of this invention is as follows.

[0012] By weight %, (1) C:0.02 - 0.40%, Si:0.01-0.60%, Mn: 0.30-2.0%, $P \leq 0.025\%$, $S \leq 0.010\%$, They are the steel materials which contained $N \leq 0.0060\%$ and $O \leq 0.0035\%$, contained REM:5-200ppm, Y:5-200 ppm and Zr:5-200 ppm % of a kind or, and two sorts or more further, and were excellent in the tempering-proof brittleness characterized by the remainder consisting of Fe and an unescapable impurity.

[0013] (2) The steel materials excellent in the tempering-proof brittleness of the preceding clause 1 publication characterized by containing a kind (aluminum:0.010-0.20%, Ti:0.005-0.08%, and calcium:0.001-0.05%) or two sorts or more, and dissolution REM:1-50ppm, Y:1-50 ppm of dissolution, a dissolution Zr:1-50ppm kind, or two sorts or more existing in the state of dissolution in steel by weight %.

[0014] (3) The steel materials excellent in tempering-proof brittleness the preceding clause 1 characterized by containing a kind (Cu:0.05-2.0% and nickel:0.05-10.0%) or two sorts and/or Cr:0.05-10.0%, Mo:0.05-2.0%, W:0.05 - 3.0%, Nb:0.005-0.10%, and V:0.01 - 0.40% of a kind or two sorts or more, and/or B:3-30 ppm by weight %, or given in two.

[0015] (4) The steel materials excellent in tempering-proof brittleness given in the preceding clauses 1 and 2 characterized by containing Ta:0.005-0.40% by weight %, or any 1 term of 3.

(5) Face manufacturing the steel which has the component of a publication in the preceding clauses 2 and 3 or any 1 term of 4. By secondary refining which follows ***** this deoxidation [weak] immediately after the weak deoxidation which adds Si or Mn at the time of tapping, or the weak deoxidation which adds a part of aluminum, aluminum, The manufacture approach of steel materials excellent in the tempering-proof brittleness characterized by adding a kind of REM, Y, and Zr, or two sorts or more after adding a kind of Ti and calcium, or two sorts or more, and carrying out hot working after casting.

[0016]

[Function] When this invention person etc. investigated minutely about the effect of tempering brittleness of low alloy steel, it found out having close relation depending on the class of chemical entity between the tempering-proof brittleness of an existence condition and low alloy steel and the hydrogen embrittlement-proof in steel. Namely, although the rare metal X centering on a lanthanoids system forms a strong nitride, a sulfide, and an oxide in steel by the Fe-P-X system (X:REM, and Y and Zr are pointed out) P centering on Dissolution X and P when it is dissolving in the metallic condition in steel, As a

result of an interaction's working among impurities, such as As and Sb, and controlling the grain boundary segregation of these impurities, while improving remarkably the tempering-proof brittleness of low alloy steel, and hydrogen embrittlement-proof Conversely, when considering as comparable tempering brittleness, the knowledge of becoming possible to ease component constraint of impurities, such as P, As, and Sb, or Si was carried out.

[0017] Here, the amount of dissolution of the metallic condition in the steel of a Fe-P-X system rare metal is based on (1) type.

Dissolution X= total X-XasX oxide-XasX nitride-XasX sulfide (Oxysulphide is included) (1)

This invention is explained below at a detail.

[0018] C was not satisfied with less than 0.02% of reinforcement, and in order to spoil base material toughness by ** 0.40%, it limited with 0.02 - 0.40%. When weldability is needed, 0.02 - 0.20% is desirable. Si was required 0.01% or more on deoxidation, and in order to spoil toughness (a base material, joint) by ** 0.60%, it limited with 0.01 - 0.60%. When the demand of tempering-proof brittleness is severe, restraining to 0.01 - 0.20% is desirable.

[0019] Mn was required 0.30% or more on reinforcement, and in order to spoil low-temperature toughness and weldability by ** 2.0%, it limited with 0.30 - 2.0%. N is limited, and the more impurities, such as P, S, N, and O, are low, the more, it is desirable, and O is limited [P] for S to 0.0035% or less 0.0060% or less 0.01% or less 0.025% or less. especially -- after a rare metal's hot-rolling -- a Fe-P-X system -- the inside of steel -- meta--- in order to dissolve in the condition [*****], S and O are so desirable that they are low, and 0.0020% or less of O is [S] desirable 0.005% or less.

[0020] REM set to 5 ppm or more, in order to secure the 1 ppm or more of the amounts of dissolution REM, and by 200 ppm **, in order to spoil the welding reactivity of cleanliness or a weld metal by inclusion, it was limited to 5-200 ppm. In addition, although REM has compounded them by the generic name of lanthanoidses, such as La and Ce, even if it carries out independent addition of La or the Ce, the effectiveness does not change at all.

[0021] Y set to 5 ppm or more, in order to secure the 1 ppm or more of the amounts of dissolution Y, and by 200 ppm **, in order to spoil the welding reactivity of cleanliness or a weld metal by inclusion, it was limited to 5-200 ppm. Zr set to 5 ppm or more, in order to secure the 1 ppm or more of the amounts of dissolution Zr, and by 200 ppm **, in order to spoil the welding reactivity of cleanliness or a weld metal by inclusion, it was limited to 5-200 ppm.

[0022] In order that an interaction might work among impurities, such as P, by the Fe-P-REM system, 1 ppm or more of dissolution REM were required, and by 50 ppm **, in order to spoil the base material toughness by REM carbide, it was limited to 1-50 ppm. In order that an interaction might work among impurities, such as P, by the Fe-P-Y system, 1 ppm or more of dissolution Y were required, and by 50 ppm **, in order to spoil the base material toughness by Y carbide, it was limited to 1-50 ppm.

[0023] In order that an interaction might work among impurities, such as P, by the Fe-P-Zr system, 1 ppm or more of dissolution Zr were required, and by 50 ppm **, in order to spoil the base material toughness by Zr carbide, it was limited to 1-50 ppm. (1) In order to be stabilized and to secure the amount of dissolution of the metallic condition in the steel of the rare metal by the formula, as stated previously, impurities, such as S, N, and O, are so desirable that they are low, but if compound addition of calcium, Ti, the aluminum, etc. is carried out, it will become much more effective.

[0024] Although aluminum was an important element on deoxidation, since deoxidation was performed by Si and Ti, in order to prevent oxidation of X (rare metal) and to secure effectively 1 ppm or more of dissolution X, it considered as 0.010% or more, and in order to spoil the welding reactivity of cleanliness or a weld metal by inclusion by ** 0.20%, it limited to 0.010 - 0.20%. calcium considered as 0.001% or more, in order to form CaS (Oxysulphide is included) and to secure effectively 1 ppm or more of dissolution X (rare metal), and in order to spoil the welding reactivity of cleanliness or a weld metal by inclusion by ** 0.05%, it was limited to 0.001 - 0.05%.

[0025] Ti formed TiN at the time of the coagulation of steel, in order to stabilize 1 ppm or more and to secure Dissolution X (rare metal), it considered as 0.005% or more, and in order to spoil joint toughness by TiC deposit by ** 0.08%, it was limited to 0.005 - 0.08%. According to the application made into the

purpose, the component design of the content of C, Si, and Mn is carried out in consideration of board thickness from need properties (reinforcement, low-temperature toughness, etc.) by the predetermined process (as [rolling], heat treatment, or TMCP). Although the quality design of the initial complement of Cu, nickel, Cr, Mo, W, Nb, V, and B other than the above-mentioned element is carried out suitably and it adds when a property with special elevated-temperature property, weldability, etc. is required, the reason for limitation is explained below.

[0026] Although Cu permuted by C, Si, and Mn for the purpose of Ceq reduction for the improvement in low-temperature toughness and it was added 0.05% or more, while hot shortness is promoted by ** 2.0% and equivalent nickel addition is needed, in order to spoil weldability, it limited to 0.05 - 2.0%. Although nickel was permuted by C, Si, and Mn for the purpose of Ceq reduction for the improvement in low-temperature toughness and it was added 0.05% or more, since the effectiveness was saturated, 10.0 super-** was limited to 0.05 - 10.0%.

[0027] Although Cr was further added 0.05% or more for improvement in a property, such as high temperature strength, for the reservation on the strength by the improvement in hardenability, since the effectiveness was saturated, 10.0% super-** was limited to 0.05 - 10.0%. Although Mo was added 0.05% or more by the on-the-strength secured pan by the improvement in hardenability for improvement in a property, such as high temperature strength, since the effectiveness was saturated, 2.0% super-** was limited to 0.05 - 2.0%.

[0028] W was required 0.05% or more to improve creep strength, and since the effectiveness was saturated, 3.0% super-** was limited to 0.05 - 3.0%. Although added 0.005% or more for the improvement in on the strength, and crystal grain control, since weldability and low-temperature toughness were spoiled by ** 0.10%, Nb was limited to 0.005 - 0.10%.

[0029] Although added 0.01% or more for the improvement in on the strength, and the improvement in a property of high temperature strength, since weldability and low-temperature toughness deteriorated in ** 0.40%, V was limited to 0.01 - 0.40%. Although added 0.005% or more for the improvement in on the strength, and improvement in high temperature strength, such as a creep, since weldability was spoiled by ** 0.40%, Ta was limited to 0.005 - 0.40%.

[0030] Especially, although it is an element effective in high-intensity-izing of extra-thick steel materials and was added by 3 ppm or more for the reservation on the strength by the hardening disposition top, since low-temperature toughness deteriorated, B was limited to 3-30 ppm by 30 ppm **. Total X is added in steel and the usual hot working, such as forging or rolling, is performed after reheating beyond the dissolution temperature of X so that the dissolution X calculated by (1) type may serve as forward from O, N, and S which contain Dissolution X (X:REM, Y or Zr) in steel in specified quantity ****. In addition, it may not be and any are sufficient, and casting does not have the limit by the existence of heat treatment of steel, and the heat treatment approach, either, and that of the limit by the steel ingot or continuous casting is good by the general approach.

[0031] Furthermore, in order to secure the amount of dissolution by which the rare metal was stabilized Although it is desirable to carry out compound addition of aluminum, calcium, Ti, etc. as mentioned above, by secondary refining, such as vacuum degassing which follows ***** this deoxidation [weak] immediately after the weak deoxidation by Si+Mn at the time of tapping, or a part of Si+Mn+aluminum, or ladle refinement, aluminum, After adding a kind of Ti and calcium, or two sorts or more, if a kind of REM, Y, and Zr or two sorts or more are added, oxide formation of a rare metal will be controlled by aluminum, sulfide formation is controlled by calcium, and since the nitridation is controlled by Ti, it becomes much more effective.

[0032]

[Example] The chemical entity of an example is shown in Table 1. A-F and K are the examples of this invention, and G-I is an example of a comparison. In detail, the example A of this invention is invention according to claim 1, and the example B of this invention is invention according to claim 2. Moreover, example C-E of this invention is invention according to claim 3 corresponding to claim 2, the example F of this invention is invention according to claim 3 corresponding to claim 1, and the example K of this invention is invention according to claim 4 corresponding to claim 2. On the other hand, the example G

of a comparison and H.I do not have addition of a rare metal, and are an example of a comparison corresponding to the examples A, E, and F of this invention, respectively.

[0033] Moreover, the example K of this invention is invention by the manufacture approach according to claim 5. That is, since Steel K has added REM after carrying out compound addition of the initial-complement whole quantity of aluminum, Ti, and calcium while performing minute amount addition of Si aiming at a quality governing, and Mn at the time of RH degasifying which follows the weak deoxidation by Si at the time of tapping, and Mn, the amount of dissolution of the rare metal in comparison with an addition (yield) is very high rather than other examples of this invention.

[0034] The quality of the material of an example is shown in Table 2. After ingoting conventionally the low alloy steel which has the component of a publication in Table 1 by the well-known approach and manufacturing the slab of 200mm thickness, it reheated at 1250 degrees C and rolled out to 50mm thickness with thick plate rolling. Then, the tensile test (JIS No. 4) and the impact test (JIS No. 4) were performed using the test piece extracted from the thick plate which performed predetermined steel plate heat treatment. On the other hand, embrittlement processing performed stress relieving annealing (SR) of 45 hours to Steel A, B, and G at 450 degrees C, and postweld heat treatment (PWHT) of 1000 hours was performed to steel C-F, K, and H-I at 480 degrees C.

[0035] The impact test (JIS No. 4) and the hydrogen embrittlement trial (WOL) were performed using the test piece extracted from the steel plate which performed these embrittlement processings. If it restrains from Table 2 to $Si \leq 0.020\%$ while this invention steel is extremely excellent in whenever [embrittlement / in / from comparison steel / an impact test] ($\Delta FATT$) with 1/2 or less, embrittlement will not be accepted at all. Furthermore, it turns out that the hydrogen embrittlement-proof (K1SCC) after performing prolonged PWHT is also excellent. That is, while improving $\Delta FATT$ and K1SCC by making a rare metal contain in the state of dissolution according to this invention, a rare metal can be made to contain in the state of dissolution effectively by carrying out compound addition with aluminum, Ti, and calcium. Therefore, according to this invention, while being able to improve the tempering-proof brittleness of low alloy steel, and hydrogen embrittlement-proof (delayed fracture-proof property), if the same quality level is aimed at, the relaxation of component constraint of impurities, such as P, or Si leading to embrittlement will be attained.

[0036]

[Table 1]

実施例の化学成分

(* : ppm、その他 : MASS%)

鋼	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	W	Nb	V
本 発 明 例	A	0.38	0.24	0.82	.020	.006	—	—	—	—	—	—
	B	0.18	0.40	1.50	.015	.005	—	—	—	—	—	—
	C	0.15	0.23	1.10	.018	.004	—	—	0.14	—	—	.040
	D	0.12	0.25	0.97	.016	.002	0.26	—	0.97	—	—	.046
	E	0.08	0.08	0.75	.014	.002	—	4.15	0.80	0.45	—	.078
	F	0.08	0.22	0.80	.019	.006	1.95	2.20	0.85	—	0.35	.040
	K	0.08	0.25	0.75	.010	.003	0.95	1.10	0.45	0.15	0.25	.020
比 較 例	G	0.36	0.26	0.85	.018	.008	—	—	—	—	—	—
	H	0.08	0.20	0.80	.016	.004	—	4.20	0.75	0.45	—	.080
	I	0.10	0.24	0.75	.014	.001	2.01	2.15	0.80	—	0.30	.045

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鋼	Ta	B	Al	Ti	Ca	REM	Y	Zr	S.REM	S.Y	S.Zr
本 発 明 例	A	—	.008	—	—	.008	—	—	14	—	—
	B	—	.028	.008	.004	—	.003	—	—	7	—
	C	8	.063	.008	.003	—	.002	.004	—	5	10
	D	8	.033	.012	.004	.002	.002	—	6	5	—
	E	—	.029	.013	.005	.002	.002	.002	5	5	4
	F	—	.006	—	—	.009	—	—	10	—	—
	K	.020	—	.065	.015	.008	.003	—	15	—	—
比 較 例	G	—	.005	—	—	—	—	—	—	—	—
	H	—	.053	.010	.004	—	—	—	—	—	—
	I	—	.007	—	—	—	—	—	—	—	—

[0037]

[Table 2]

実施例の材質

鋼		鋼板厚	熱処理	Y S MPa	T S MPa	F A T T	Δ F A T T	K_{Isc} (MPa · m ^{1/2})
本 発 明 例	A	50mm	N-SR	396	581	+ 20℃	15 ℃	—
	B	50mm	N-SR	378	526	- 20℃	15 ℃	—
	C	50mm	Q T	466	617	- 65℃	10 ℃	—
	D	50mm	Q T	733	814	- 80℃	10 ℃	—
	E	50mm	Q T	807	868	- 100℃	0 ℃	45
	F	50mm	Q T	707	848	- 95℃	20 ℃	—
	K	50mm	Q T	781	885	- 90℃	10 ℃	40
比 較 例	G	50mm	N-SR	371	598	+ 15℃	40 ℃	—
	H	50mm	Q T	798	871	- 105℃	60 ℃	22
	I	50mm	Q T	714	936	- 90℃	50 ℃	—

熱処理 N-SR : 910 °C×2Hr + 625 °C×9hr

Q T : 910 °C×1Hr + 650 °C×1hr

脆化度 F A T T : 脆化処理前 (Q T, N-SRのまま) の衝撃試験破面遷移温度

$\Delta F A T T : F A T T - F A T T'$

F A T T' : 脆化処理後 (P W H T, S R) における衝撃試験破面遷移温度

K_{Isc} : 脆化処理後の水素ガス (1 気圧) 中における応力拡大係数
(Stress Intensity)

[0038]

[Effect of the Invention] As explained in full detail above, according to this invention, it sets to the steel materials of a Fe-P-X system (rare metals, such as RX:EM, or Y, Zr). P centering on X and P which dissolved in steel at supersaturation when X was made to contain in the state of metallic dissolution in steel, The result by which an interaction works among impurities, such as As and Sb, and the grain boundary segregation of these impurities is controlled among, While becoming possible to be able to raise sharply tempering-proof brittleness and hydrogen embrittlement-proof, and to correspond to strict-ization of the embrittlement criteria accompanying aggravation of strict-izing of the safety design of the large-sized structure, and global environment problems in this way Relaxation of component constraint, such as an impurity and Si, is attained to a demand of the same embrittlement criteria.

[0039] Therefore, since the improvement in dependability of the large-sized structure can bring about improvement in time-necessary-for-completion-nonprice competitiveness with improvement in saving resources and energy-saving-price competitiveness from the first by this invention, this invention can say that it is about the thing which has industrially very remarkable economic earnings and which is given to the industrial world.

[Translation done.]

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(54)【発明の名称】 耐焼戻し脆性に優れた鋼材及びその製造方法

(57)【要約】

【目的】 P、Sb、As等の不純物の粒界偏析を防止して耐焼戻し脆性に優れた鋼材を提供する。

【構成】 C、Si、Mn、P、S、N、Oを含有する鋼において、REM、Y、Zrの一種又は二種以上を5～200ppm含有することを特徴とする耐焼戻し脆性に優れた鋼材。この鋼材に必要な応じてAl、Ti、Caの一種又は二種以上を含有させることにより、固溶REM、固溶Y、固溶Zrの一種又は二種以上を1～50ppm固溶状態で存在させる。これらの鋼材は必要に応じてCu、Ni、Cr、Mo、W、Nb、V、Ta、Bの一種又は二種以上を含有し得る。前記鋼材を製造するに際して、Si、Mn、Alの一部による弱脱酸後にAl、Ti、Caの一種又は二種以上を添加し、次いでREM、Y、Zrの一種又は二種以上を添加することを特徴とする耐焼戻し脆性に優れた鋼材の製造方法。

【特許請求の範囲】

【請求項1】 重量%で、

C: 0.02~0.40%、Si: 0.01~0.60%、Mn: 0.30~2.0%、P≤0.025%、S≤0.010%、N≤0.0060%、O≤0.0035%を含有し、

さらに、REM: 5~200ppm、Y: 5~200ppm及びZr: 5~200ppm%の一種又は二種以上を含有し、

残部はFe及び不可避的不純物からなることを特徴とする耐焼戻し脆性に優れた鋼材。

【請求項2】 重量%で、

Al: 0.010~0.20%、Ti: 0.005~0.08%及びCa: 0.001~0.05%の一種又は二種以上を含有し、

固溶REM: 1~50ppm、固溶Y: 1~50ppm及び固溶Zr: 1~50ppmの一種又は二種以上が鋼中に固溶状態で存在することを特徴とする請求項1記載の耐焼戻し脆性に優れた鋼材。

【請求項3】 重量%で、Cu: 0.05~2.0%及びNi: 0.05~10.0%の一種又は二種及び又はCr: 0.05~10.0%、Mo: 0.05~2.0%、W: 0.05~3.0%、Nb: 0.005~0.10%及びV: 0.01~0.40%の一種又は二種以上及び又はB: 3~30ppmを含有することを特徴とする請求項1又は2記載の耐焼戻し脆性に優れた鋼材。

【請求項4】 重量%で、Ta: 0.005~0.40%を含有することを特徴とする請求項1、2又は3のいずれか1項に記載の耐焼戻し脆性に優れた鋼材。

【請求項5】 請求項2、3又は4のいずれか1項に記載の成分を有する鋼を製造するに際して、出鋼時におけるSi若しくはMnを添加する弱脱酸、又はAlの一部を添加する弱脱酸後直ちに又は当該弱脱酸に引き続く二次精練でAl、Ti、Caの一種又は二種以上を添加した後にREM、Y、Zrの一種又は二種以上を添加し、鍛造後に熱間加工することを特徴とする耐焼戻し脆性に優れた鋼材の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は耐焼戻し脆性に優れた低合金鋼及びその製造方法に関するものである。詳しくは圧延、鍛造、鍛造によって製造される低合金鋼の熱処理時の脆化及びその鋼材を用いての压力容器、化学容器、橋梁、機械部品、海洋構造物等の構造物への鋼材加工時における溶接後熱処理（及び曲げ加工物の焼戻し、応力除去焼鈍等）による脆化又は高温使用時の使用中脆化の抑制に関するものである。

【0002】

【従来の技術】近年化学技術の進歩に従い、化学反応容

器、压力容器等は次第に大型化される傾向にあり、又使用される環境も益々過酷なものになっている。従って、鋼材に要求される性質、就中、焼戻し脆性の抑制に対する要求は鋼材の厚肉化に伴う溶接後熱処理（応力除去焼鈍）の長時間化、使用温度の高温化により極めて厳しくなり、その対策が困難になっているのが実状である。

【0003】焼戻し脆性、水素脆性を抑制する従来の技術としては特開昭55-91962号公報、特開昭56-58952号公報、特開昭57-29553号公報に記載の提案がある。又、固溶REM、固溶Y、固溶Zrを添加する従来技術としては特願平6-198830号による提案がある。特開昭55-91962号公報記載の提案は、Ni系調質鋼に固溶メタリックAlを0.15%以上含有させ、粒界におけるSiと固溶Alとのサイトコンペティションにより耐焼戻し脆性と耐水性脆性の改善を図るものである。

【0004】特開昭56-58952号公報記載の提案は、特定成分の低合金鋼に、Zr又はCaの鋼中Sによって消費される量以上の限定量を含有させることにより耐焼戻し脆性を改善するものである。特開昭57-29553号公報記載の提案は、特定成分の低合金鋼にCaを20~100ppm含有させることにより耐焼戻し脆性を改善するものである。

【0005】特願平6-198830号における提案は、特定成分の低合金鋼にREM、Y又はZrを添加してそれらの固溶量を限定することにより水素性欠陥の発生を抑制して鋼材の内部品質を改善するものである。

【0006】

【発明が解決しようとする課題】特開昭55-91962号公報には固溶メタリックAlによってNi系調質鋼の焼戻し脆性が改善されるという記載はあるものの、REM、Y、Zrに関する技術の開示が全くないばかりか、固溶REM、固溶Y、固溶Zrが焼戻し脆性を改善する記載は全くない。従って、前記課題を解決する技術思想は全く含まれておらず、前記課題はそのまま取り残されているのが実状である。

【0007】特開昭56-58952号公報にはZr又はCaの鋼中Sによって消費される量以上の限定量により低合金鋼の耐焼戻し脆性が改善される記載があるものの、REM、Yに関する技術の開示は全くないばかりか、Zrに関してもO、NによるZrの消費を補償する思想が欠落しており、且つ固溶REM、固溶Y、固溶Zrが低合金鋼の耐焼戻し脆性を改善するという記載は全くない。従って、前記課題を解決する技術思想は全く含まれておらず、前記課題はそのまま取り残されているのが実状である。

【0008】特開昭57-29553号公報にはCaによって低合金鋼の耐焼戻し脆性が改善される記載はあるものの、REM、Y、Zrに関する技術の開示が全くないばかりか、固溶REM、固溶Y、固溶Zrが耐焼戻し

脆性を改善する記載は全くない。従って、前記課題を解決する技術思想は全く含まれておらず、前記課題はそのまま取り残されているのが実状である。

【0009】特願平6-198830号にはREM、Y、Zrの鋼中S、O、Nによって消費される量以上の限定量により低合金鋼の内分品質が改善される記載はあるものの、耐焼戻し脆性に関する技術の開示は全くないばかりか、REM、Y、Zrの消費に関してもO、Nによる消費を補償するO及びNの限定が特許請求の範囲になく固溶量を厳密に制御する思想は不十分であり、且つ固溶REM、固溶Y、固溶Zrが低合金鋼の耐焼戻し脆性を改善する記載は全くない。従って、前記課題を解決する技術思想は全く含まれておらず、前記課題はそのまま取り残されているのが実状である。

【0010】本発明は前記した低合金鋼における耐焼戻し脆性及び耐水素脆性を大幅に向上するとともに、さらに焼戻し脆性に関するP等不純物やSiの成分制約を緩和して成分設計の自由度を大きくすることを目的とする。

【0011】

【発明が解決するための手段】本発明者等が低合金鋼の焼戻し脆性について仔細に調査したところ、鋼中に固溶するREM、Y、Zrの固溶量と耐焼戻し脆性は極めて深い関係を有するとともに水素脆性をも改善することを新たに知見するに至った。本発明の要旨とするところは下記のとおりである。

【0012】(1)重量%で、C:0.02~0.40%、Si:0.01~0.60%、Mn:0.30~2.0%、P≤0.025%、S≤0.010%、N≤0.0060%、O≤0.0035%を含有し、さらに、REM:5~200ppm、Y:5~200ppm及びZr:5~200ppm%の一種又は二種以上を含有し、残部はFe及び不可避的不純物からなることを特徴とする耐焼戻し脆性に優れた鋼材。

【0013】(2)重量%で、Al:0.010~0.20%、Ti:0.005~0.08%及びCa:0.001~0.05%の一種又は二種以上を含有し、固溶REM:1~50ppm、固溶Y:1~50ppm及び固溶Zr:1~50ppmの一種又は二種以上が鋼中に*

固溶X=トータルX-XasX酸化物-XasX窒化物-XasX硫化物(O

xy sulphideを含む)

以下に本発明を詳細に説明する。

【0018】Cは0.02%未満では強度を満足せず、0.40%超では母材靱性を損なうために0.02~0.40%と限定した。溶接性が必要とされる時には0.02~0.20%が好ましい。Siは脱酸上0.01%以上必要で、0.60%超では靱性(母材、継手)を損なうために0.01~0.60%と限定した。耐焼戻し脆性の要求が厳しい時には、0.01~0.20%に制約することが好ましい。

* 固溶状態で存在することを特徴とする前項1記載の耐焼戻し脆性に優れた鋼材。

【0014】(3)重量%で、Cu:0.05~2.0%及びNi:0.05~10.0%の一種又は二種及び/又はCr:0.05~10.0%、Mo:0.05~2.0%、W:0.05~3.0%、Nb:0.005~0.10%及びV:0.01~0.40%の一種又は二種以上及び/又はB:3~30ppmを含有することを特徴とする前項1又は2記載の耐焼戻し脆性に優れた鋼材。

【0015】(4)重量%で、Ta:0.005~0.40%を含有することを特徴とする前項1、2又は3のいずれか1項に記載の耐焼戻し脆性に優れた鋼材。

(5)前項2、3又は4のいずれか1項に記載の成分を有する鋼を製造するに際して、出鋼時におけるSi若しくはMnを添加する弱脱酸、又はAlの一部を添加する弱脱酸後直ちに又は当該弱脱酸に引き続く二次精錬でAl、Ti、Caの一種又は二種以上を添加した後にREM、Y、Zrの一種又は二種以上を添加し、鍛造後に熱間加工することを特徴とする耐焼戻し脆性に優れた鋼材の製造方法。

【0016】

【作用】本発明者等が低合金鋼の焼戻し脆性の影響に関して仔細に調査したところ、化学成分の種類によっては鋼中における存在状態と低合金鋼の耐焼戻し脆性及び耐水素脆性との間に密接な関係を有することを見出した。即ち、Fe-P-X系(X:REM、Y、Zrを指す)ではランタノイド系を中心とする希少金属Xは鋼中で強い窒化物、硫化物、酸化物を形成するが、鋼中にメタリックな状態で固溶していると、固溶XとPを中心とするP、As、Sb等の不純物との間に相互作用が働いて、これら不純物の粒界偏析が抑制される結果、低合金鋼の耐焼戻し脆性及び耐水素脆性を著しく向上するとともに、逆に同程度の焼戻し脆性とする場合にはP、As、Sb等の不純物やSiの成分制約を緩和することが可能になることを知見した。

【0017】ここで、Fe-P-X系希少金属の鋼中におけるメタリックな状態の固溶量は(1)式による。

(1)

※【0019】Mnは強度上0.30%以上必要で2.0%超では低温靱性、溶接性を損なうために0.30~2.0%と限定した。P、S、N、O等の不純物は低ければ低いほど好ましく、Pは0.025%以下、Sは0.01%以下、Nは0.0060%以下、Oは0.0035%以下に限定される。特に、希少金属が熱間圧延後にFe-P-X系で鋼中にメタリックな状態で固溶するためにはS、Oは低いほど望ましく、Sは0.005%以下、Oは0.0020%以下が好ましい。

※50

【0020】REMは固溶REM量を1ppm以上確保するために5ppm以上とし、200ppm超では介在物による清浄度や溶接金属の溶接反応性を損なうために、5～200ppmに限定した。尚、REMはLa、Ce等のランタノイド元素の総称でそれらを複合しているが、La又はCeを単独添加してもその効果は全く変わらない。

【0021】Yは固溶Y量を1ppm以上確保するために5ppm以上とし、200ppm超では介在物による清浄度や溶接金属の溶接反応性を損なうために、5～200ppmに限定した。Zrは固溶Zr量を1ppm以上確保するために5ppm以上とし、200ppm超では介在物による清浄度や溶接金属の溶接反応性を損なうために、5～200ppmに限定した。

【0022】固溶REMはFe-P-REM系でP等不純物との間に相互作用が働くために1ppm以上必要で、50ppm超ではREM炭化物による母材靱性を損なうために、1～50ppmに限定した。固溶YはFe-P-Y系でP等不純物との間に相互作用が働くために1ppm以上必要で、50ppm超ではY炭化物による母材靱性を損なうために、1～50ppmに限定した。

【0023】固溶ZrはFe-P-Zr系でP等不純物との間に相互作用が働くために1ppm以上必要で、50ppm超ではZr炭化物による母材靱性を損なうために、1～50ppmに限定した。(1)式による希少金属の鋼中におけるメトリックな状態の固溶量を安定して確保するには、先に述べた如くS、N、O等の不純物は低いほど好ましいが、Ca、Ti、Al等を複合添加すると一層効果的となる。

【0024】Alは脱酸上重要な元素であるがSiやTiによっても脱酸が行われるので、X(希少金属)の酸化を防止して固溶Xを1ppm以上効果的に確保するために0.010%以上とし、0.20%超では介在物による清浄度や溶接金属の溶接反応性を損なうために、0.010～0.20%に限定した。CaはCaS(Oxysulphideを含む)を形成して固溶X(希少金属)を1ppm以上効果的に確保するために0.001%以上とし、0.05%超では介在物による清浄度や溶接金属の溶接反応性を損なうために、0.001～0.05%に限定した。

【0025】Tiは鋼の凝固時にTiNを形成して固溶X(希少金属)を1ppm以上安定して確保するために0.005%以上とし、0.08%超ではTiC析出により継手靱性を損なうために、0.005～0.08%に限定した。C、Si、Mnの含有量は目的とする用途に応じて、所定の製法(圧延まや熱処理又はTMC P)で必要特性(強度及び低温靱性等)から板厚を考慮して成分設計される。高温特性や溶接性等の特別な特性が必要な場合には上記元素の他にCu、Ni、Cr、Mo、W、Nb、V、Bの必要量を適宜品質設計して添加

するが、以下にその限定理由を述べる。

【0026】Cuは低温靱性向上のためCe q低減を目的としてC、Si、Mnに置換して0.05%以上添加されるが、2.0%超では熱間脆性を助長し等量のNi添加が必要となるとともに溶接性を損なうために0.05～2.0%に限定した。Niは低温靱性向上のためCe q低減を目的としてC、Si、Mnに置換して0.05%以上添加されるが、10.0%超ではその効果が飽和するために、0.05～10.0%に限定した。

【0027】Crは焼入性向上による強度確保のため、さらには高温強度等の特性向上のために0.05%以上添加されるが、10.0%超ではその効果が飽和するために、0.05～10.0%に限定した。Moは焼入性向上による強度確保さらには高温強度等の特性向上のために0.05%以上添加されるが、2.0%超ではその効果が飽和するために、0.05～2.0%に限定した。

【0028】Wはクリープ強度を向上するには0.05%以上必要で、3.0%超ではその効果が飽和するために、0.05～3.0%に限定した。Nbは強度向上及び結晶粒制御のために0.005%以上添加されるが、0.10%超では溶接性、低温靱性が損なわれるために、0.005～0.10%に限定した。

【0029】Vは強度向上及び高温強度の特性向上のために0.01%以上添加されるが、0.40%超では溶接性、低温靱性が劣化するために、0.01～0.40%に限定した。Taは強度向上及びクリープ等の高温強度向上のために0.005%以上添加されるが、0.40%超では溶接性が損なわれるために、0.005～0.40%に限定した。

【0030】Bは特に極厚鋼材の高強度化に有効な元素で、焼入れ性向上による強度確保のために3ppm以上添加されるが、30ppm超では低温靱性が劣化するために、3～30ppmに限定した。固溶X(X:REM、YまたはZr)を所定量得るには、鋼中に含有されるO、N、Sから(1)式により計算される固溶Xが正となるように、トータルXを鋼中に添加しXの固溶温度以上に再加熱後、鍛造又は圧延等の通常の熱間加工を行う。尚、鍛造は鋼塊又は連続鍛造による制限はなくいつでも良く、鋼の熱処理の有無、熱処理方法による制限もなく一般的な方法でよい。

【0031】さらに、希少金属の安定した固溶量を確保するには、前述した如くAl、Ca、Ti等を複合添加するのが好ましいが、出鋼時におけるSi+Mn又はSi+Mn+Alの一部による弱脱酸後直ちに又は当該弱脱酸に引き続く真空脱ガス又は取鍋精錬等の二次精錬でAl、Ti、Caの一種又は二種以上を添加した後に、REM、Y、Zrの一種又は二種以上を添加すると希少金属の酸化物形成はAlにより抑制され、硫化物形成はCaにより抑制され、窒化物形成はTiにより抑制され

るために一層効果的になる。

【0032】

【実施例】表1に実施例の化学成分を示す。A～F、Kが本発明例であり、G～Iが比較例である。詳しくは、本発明例Aは請求項1記載の発明であり、本発明例Bは請求項2記載の発明である。又、本発明例C～Eは請求項2に対応した請求項3記載の発明であり、本発明例Fは請求項1に対応した請求項3記載の発明であり、本発明例Kは請求項2に対応した請求項4記載の発明である。一方、比較例G、H、Iは希少金属の添加がなく、

本発明例A、E、Fにそれぞれ対応する比較例である。【0033】又、本発明例Kは請求項5記載の製造方法による発明である。即ち、鋼Kは出鋼時のSi、Mnによる弱脱酸に引き続くRH脱ガス時において成分調整を目的としたSi、Mnの微量添加を行うとともにAl、Ti、Caの必要量全量を複合添加した後にREMを添加しているために、他の本発明例よりも添加量に比べた希少金属の固溶量（歩留）が極めて高くなっている。

【0034】表2に実施例の材質を示す。表1に記載の成分を有する低合金鋼を従来公知の方法で溶製し200mm厚のスラブを製造した後に、1250℃に再加熱して厚板圧延により50mm厚に圧延を行った。その後、所定の鋼板熱処理を行った厚板から採取した試験片を用

いて引張り試験（JIS4号）及び衝撃試験（JIS4号）を行った。一方、脆化処理は鋼A、B、Gには450℃で45時間の応力除去焼鈍（SR）を行い、鋼C～F、K、H～Iには480℃で1000時間の溶接後熱処理（PWHT）を行った。

【0035】これらの脆化処理を行った厚鋼板から採取した試験片を用いて衝撃試験（JIS4号）及び水素脆化試験（WOL）を行った。表2より本発明鋼は比較鋼よりも衝撃試験における脆化度（ $\Delta FATT$ ）が1/2以下と極めて優れているとともにSi \leq 0.020%に制約すれば脆化は全く認められない。さらに、長時間のPWHTを行った後の耐水素脆性（ K_{ISCC} ）も優れていることが分かる。即ち、本発明に従い希少金属を固溶状態で含有させることにより $\Delta FATT$ 及び K_{ISCC} を改善するとともに、Al、Ti、Caと複合添加することにより希少金属を効果的に固溶状態で含有させることができる。従って、本発明によれば、低合金鋼の耐焼戻し脆性、耐水素脆性（耐遅れ破壊特性）を向上することができるとともに、同一の品質水準を狙うならば脆化の原因となるP等の不純物やSiの成分制約の緩和が可能となる。

【0036】

【表1】

9
実施例の化学成分

10
(*: ppm、その他: MASS%)

鋼	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	W	Nb	V
本 発 明 例	A	0.38	0.24	0.82	.020	.006	—	—	—	—	—	—
	B	0.18	0.40	1.50	.015	.005	—	—	—	—	—	—
	C	0.15	0.23	1.10	.018	.004	—	—	0.14	—	—	.040
	D	0.12	0.25	0.97	.016	.002	0.26	—	0.97	—	—	.046
	E	0.08	0.08	0.75	.014	.002	—	4.15	0.80	0.45	—	.078
	F	0.08	0.22	0.80	.019	.006	1.95	2.20	0.85	—	0.35	.040
	K	0.08	0.25	0.75	.010	.003	0.95	1.10	0.45	0.15	0.25	.040
比 較 例	G	0.36	0.26	0.85	.018	.008	—	—	—	—	—	—
	H	0.08	0.20	0.80	.016	.004	—	4.20	0.75	0.45	—	.080
	I	0.10	0.24	0.75	.014	.001	2.01	2.15	0.80	—	0.30	.045

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鋼	Ta	B	Al	Ti	Ca	REM	Y	Zr	S.REM	S.Y	S.Zr
本 発 明 例	A	—	.008	—	—	.008	—	—	14	—	—
	B	—	.028	.008	.004	—	.003	—	—	7	—
	C	8	.063	.003	.003	—	.002	.004	—	5	10
	D	8	.033	.012	.004	.002	.002	—	6	5	—
	E	—	.029	.013	.005	.002	.002	.002	5	5	4
	F	—	.006	—	—	.009	—	—	10	—	—
	K	.020	—	.065	.015	.008	.003	—	15	—	—
比 較 例	G	—	.005	—	—	—	—	—	—	—	—
	H	—	.053	.010	.004	—	—	—	—	—	—
	I	—	.007	—	—	—	—	—	—	—	—

【0037】

* 30 * 【表2】

1 1
実 施 例 の 材 質

1 2

鋼		鋼板厚	熱処理	YS MPa	TS MPa	FATT	ΔFATT	K_{Isc} (MPa \cdot m ^{1/2})
本 発 明 例	A	50mm	N-SR	396	581	+ 20℃	15 ℃	-
	B	50mm	N-SR	378	526	- 20℃	15 ℃	-
	C	50mm	QT	466	617	- 65℃	10 ℃	-
	D	50mm	QT	733	814	- 80℃	10 ℃	-
	E	50mm	QT	807	868	- 100℃	0 ℃	45
	F	50mm	QT	707	848	- 95℃	20 ℃	-
	K	50mm	QT	781	885	- 90℃	10 ℃	40
比 較 例	G	50mm	N-SR	371	598	+ 15℃	40 ℃	-
	H	50mm	QT	798	871	- 105℃	60 ℃	22
	I	50mm	QT	714	936	- 90℃	50 ℃	-

熱処理 N-SR : 910 ℃×2hr +625 ℃×9hr

QT : 910 ℃×1hr +650 ℃×1hr

脆化度 FATT : 脆化処理前 (QT, N-SR のまま) の衝撃試験破面遷移温度

 $\Delta FATT : FATT - FATT'$

FATT' : 脆化処理後 (PWHT, SR) における衝撃試験破面遷移温度

 K_{Isc} : 脆化処理後の水素ガス (1 気圧) 中における応力拡大係数
(Stress Intensity)

【0038】

【発明の効果】以上詳述した如く、本発明に従い Fe-P-X 系 (RX : EM 又は Y、Zr 等の希少金属) の鋼材において、X を鋼中にメトリックな固溶状態で含有させると、鋼中に過飽和に固溶された X と P を中心とする P、As、Sb 等の不純物との間に相互作用が働いてこれら不純物の粒界偏析が抑制される結果、耐焼戻し脆性及び耐水素脆性を大幅に向上させることができ、かくして大型構造物の安全設計の厳格化、地球環境問題の深刻*

* 化に伴う脆化基準の厳格化に対応することが可能になるとともに、同一の脆化基準の要求に対しては不純物や Si 等の成分制約の緩和が可能となる。

【0039】従って、本発明により大型構造物の信頼性向上はもとより省資源、省エネルギー的価格競争力の向上とともに工期的非価格競争力の向上をもたらすことができるので、本発明が産業界に与える工業的ならびに経済的利益はきわめて顕著なものであるといえる。

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